“High Frequency Dielectric Study on the Hydrogen Bonding Interaction on Diol”

Synopsis

Submitted to

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For the registration of the topic for
Doctor of Philosophy

In the Subject of
PHYSICS

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By

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Abstract of proposed work plan/problem

"High Frequency Dielectric Study on the Hydrogen Bonding Interaction on Diol"

1. Introduction

The intermolecular attractive forces in liquids play a crucial role in the formation of solution. When solute dissolves in solvent, molecules of the solute disperse throughout the solvent. The solute-solvent interacts in such a way that solute molecules occupy positions that normally taken by solvent molecules. The ease with which solute molecules take over solvent molecules depends on the relative strength of three types of interactions

a) Solvent - solvent

b) Solute - solute

c) Solvent – solute

Whenever a solution contains molecules with an electropositive hydrogen atom and with an electronegative atom (such as nitrogen, chlorine, oxygen, sulfur, or fluorine), hydrogen bonding may occur, whereas the properties of the solution are affected profoundly. Hydrogen bonds may form between similar molecules or between dissimilar molecules.

Aim of present work is devoted to study dielectric relaxation of diol using TDR technique. Diols are the organic compounds which are most important in the field of organic chemistry

and biochemistry. Due to the presence of two –OH groups in a diol molecule, the solution chemistry of these compounds can be strongly influenced by the intermolecular and intramolecular hydrogen bond formation. It also plays an important role in the physical properties of the molecules. Diols have many industrial and biological applications [1-3].

For collecting all the information about solute-solvent interaction one need to do spectroscopy. Spectroscopy is defined as interaction of radiation with matter. For gathering the information about any substance, spectroscopy is very useful technique. According to the size, shape and nature of the substance there are various types of spectroscopies. One of them is dielectric relaxation spectroscopy, which gives the information about mechanism of dielectric materials. Dielectric materials are bad conductor of electricity and heat but they can endure the electric field within them for long time. When electric field is applied across the dielectric material, it is polarized and electric field persists within them.

Dielectric relaxation spectroscopy is occupied very large range of frequency band i.e. from 10^{-4} Hz to 10^{12} Hz therefore it is also known as 'Broadband dielectric spectroscopy'. Dielectric relaxation spectroscopy is sensitive to relaxation process in an extremely wide range of characteristic time i.e. 10^{5} – 10^{-12} (seconds). This spectroscopy has many applications in various fields [4]. By using this spectroscopy, we can understand the liquid dynamics, charge distribution, orientation of molecules and solute-solvent interaction within binary and ternary mixtures [5-7].

2. Literature Review and Development in the Subject(previous work done in the relevant area):

Over the past few years, considerable experimental studies about the dielectric relaxation behavior of liquids solutions of alkyl (R) and aryl (Ar) molecules have been reported. The dielectric relaxation measurement addresses the useful information on the water structure in aqueous systems [8-29]. Bertolini *et. al.* [22] have been discussed the problems in TDR measurements and its solutions. Mehrotra *et.al*. [23] also developed the TDR measurement in India for the measurement of polar and non polar solutions. The associating behavior of alcohols in aqueous and non-aqueous solution is extensively studied through the dielectric properties, heterogeneous interactions and cooperative domains (CD) [24-29]. Many workers have reported dielectric relaxation studies of binary mixtures to understand hydrogen bonding and intramolecular rotations in the mixtures. Kadam *et al.*[30] have studied dielectric properties of 1,3 butanediol-water mixture in frequency range of 10 MHz to 30 GHz using a time domain reflectometry (TDR) technique at 25^0C temperature. Shinde *et al*. [31] have reported dielectric spectra of 1,3-propanediol-dioxane mixture in the frequency range 10 MHz to 30 GHz at 25^0C using the method of time domain reflectometry.

3. Objective of research/Proposed Hypothesis:

It is planned to carry out high frequency dielectric measurements of diol solutions using time domain dielectric relaxation spectroscopy technique having frequency range 10MHz to 50GHz at different temperature for following systems.

(i) Ethylene Glycol-Dioxane

(ii) Propanediol-Dioxane

(iii) Butanediol-Dioxane

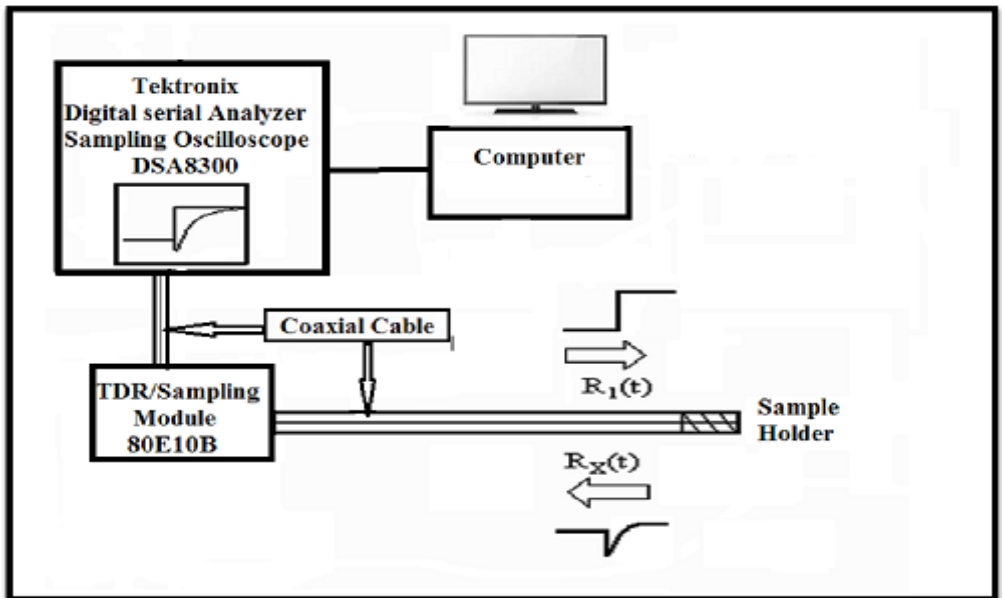
(iv) Pentanediol-Dioxane

Therefore, present objective of the work is to study the Diol solutions and determine the following parameters:

- To determine complex permittivity of diols using Time Domain Reflectometry Technique from 10 MHz to 50 GHz.
- To determine dielectric constant, dielectric loss and relaxation time at high frequency.
- To study molecular interaction and hydrogen bonding of solvents through various parameters like Krikwood correlation factor, Bruggman factor, Thermodynamic Parameters, Excess parameters etc. using picoseconds dielectric relaxation spectroscopy

4. Methodology to be adopted:

The complex dielectric spectra will be obtained by the time domain reflectometry (TDR) technique. The Tektronix model no. DSA8300 Digital Serial Analyzer sampling mainframe along with the sampling module will be used for the time domain reflectometery (TDR). Figure 1 shows experimental setup for TDR. A repetitive fast rising 250mV voltage pulse of 200 KHz with 12ps incident and 15ps reflected rise time was fed through coaxial line system of impedance 50 ohm. Sampling oscilloscope monitors changes in step pulse after reflection from the end of line. Reflected pulse without sample $R_1(t)$ and with sample $R_x(t)$ will be recorded in time window of 5ns and digitized in 2000 points is shown in figure 2.



(a)

(b)

Fig1. (a)Block diagram of Time Domain Reflectometry. (b) Photograph of TDR.

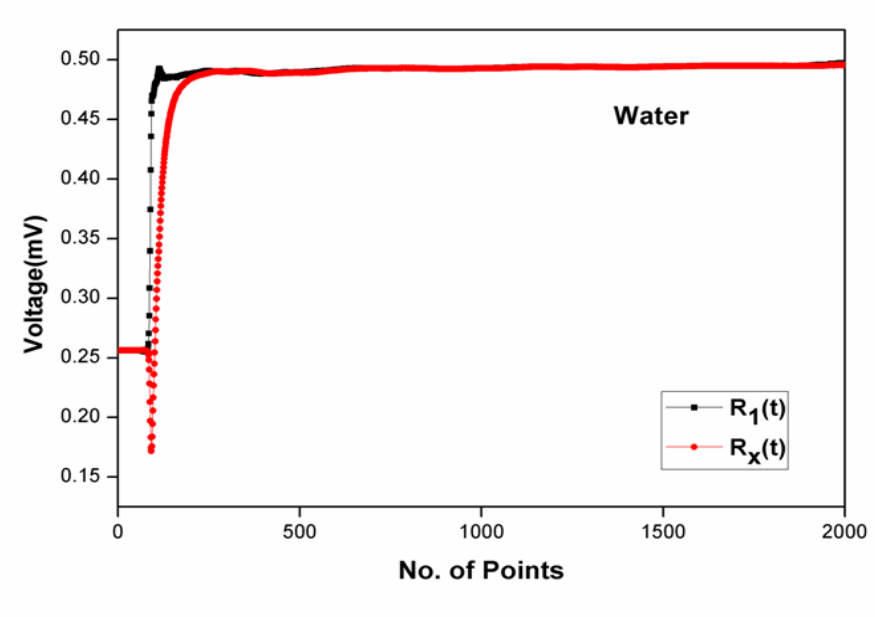


Fig.2 Reflected pulse without sample $R_1(t)$ & sample $R_x(t)$.

These pulses are added *[q(t) = $R_1(t)$ + $R_X(t)$]* and subtracted *[p(t) = $R_1(t)$ - $R_X(t)$]*. Further, the time domain data will be converted to frequency domain using Fourier transformation. Summation and Samulon methods will be used to obtain the Fourier transformation of p(t) and q(t), respectively, up to 50GHz and the frequency dependent complex reflection coefficient spectra ρ*(ω) calculated using [14].

$$\rho^{*}(\omega) = \frac{c}{j\omega d}\frac{p(\omega)}{q(\omega)} \tag{1}$$

where c is velocity of light in mm/ps, w is angular frequency, d is effective pin length.

The complex permittivity spectra $\varepsilon^*(\omega)$ was obtained from complex reflection spectra $\rho^*(\omega)$ by using bilinear calibration method given by

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{[(1+(j\omega\tau)^{1-\alpha}]^{\beta}} \tag{2}$$

where ε_0 is the static dielectric constant, ε_∞ is the permittivity at high frequency, τ is the relaxation time. The α and β are symmetric and asymmetric distribution of relaxation times, respectively. The Havriliak-Negami equation involves three relaxation models as limiting form

1) If α =0 and β=1 then single Debye relaxation.

2) $0 \leq \alpha \leq 1$ then it would be a Cole-Cole model of symmetric distribution of relaxation times.

3) α =0 and β varied such that $0 \leq \beta \leq 1$, this behavior is identified as Cole-Davidson (CD) asymmetric distribution of relaxation times.

5. Importance of study/society application

During past few year interest in liquid structure has grown rapidly, not only because of academic curiosity but also because of practical aspect that call for a fundamental understanding in terms of intermolecular interactions of water and solute. The high frequency process reflecting to depolarization comes from diffuse rotation of water molecules in making/breaking process of molecular cluster.

- **International/National status**: The following scientists are actively doing research in this field at international/National level:

  1. N Shiyanshiki, University of Tokyo, Japan.
  2. S Yaghara, University of Tokyo, Japan
  3. S Sudo, dept. of Physics, Tokyo city University, Tamazustumi, Setagaya, Tokyo,
  4. A Catldo, university di Lecce, via Monteroni, 73100 Lecce, Italy
  5. S.C. Mehrotra, Dr. BAMU, Aurangabad(MS).
  6. R.J. Sengwa, Jodhpur, JNV University, Jodhpur(RS).

- **Significance of the study:**

The dielectric and structural relaxation measurements of solution using a TDR make an immense impact on the fundamental study. The present study is devoted to dielectric and structural relaxation in dioxane using TDR technique from 10MHz to 50GHz. from dielectric relaxation parameters; one can understand orientation and hydrogen bonding interaction of diol through solute-solvent interactions.

6. Proposed work plan/Formulation and structure of study:

First Year:

(i) Literature survey on diol and related to the topic

(ii) Course Work as per university syllabus

(iii) Literature Review system to be studied.

Second Year

(i)Measurement and Training for Dielectric and spectroscopic Technique and analysis of dielectric data

(ii) Extract the dielectric parameters

(iii)Dielectric measurement of diol solutions.

(iv)Extract the dielectric parameters such as static dielectric constant, relaxation time, dielectric constant at high frequency and Kirkwood correlation factor.

Third Year:

Study the dielectric and structural behavior of diol through the dielectric relaxation parameters.

7. References

1. U Kaatze J. Mol. Liq. 56 95 (1993)

2. S D Chavan, A C Kumbharkhane, and S C Mehrotra J. Chin.Chem. Soc. 54 1457 (2007)

3. P Petong, R Pottel and U Kaatze J. Phys. Chem. A 104 7420 (2000)

4. F Kremer, A Schönhals. *'Broadband Dielectric Spectroscopy'*, Springer 2003.

5. SC Mehrotra, AC Kumbharkhane & AS Chaudhari. *'Binary Polar Liquids'*, Elsevier (2017).

6. NK Karthick, G Arivazhagan, AC Kumbharkhane et.al. *J. Mol. Structure*, 1108, 20 (2016).

7. DJS Anand Karunakaran, T Ganesh, M Maria Sylvester et.al. *Fluid Phase Equilibria,* 382 300 (2014).

8. JB Hasted. '*Aqueous dielectrics',* Chapman and Hall London (1973)

9. SD Shirgire, RB Talware, SS Kadam et.al. *J. of Mol. Liq*. 169 33 (2012).

10. AC Kumbharkhane, YS Joshi, SC Mehrotra et.al. *Physica B,* 421 1 (2013)

11. RJ Sengwa & K Kulvinder. *Indian J. of Biochem. & Biophy.* 36 325 (1999)

12. N Shinyashiki, N Ashaka, S Mashimo et.al. *J. Chem. Phys.* 93 760 (1990)

13. N Shinyashiki, S Sudo, W Abe et.al. *J. Chem. Phys.* 109 9843 (1998)

14. N Shinyashiki, I Arita, S Yagihara et.al.*J. Chem. Phys.* B102 3429 (1998)

15. N Shinyashiki and S Yagihara *J. Phys. Chem.* B103 4481 (1999)

16. KS Kanse, SD Chavan, AC Kumbharkhane et.al. *J. Poly. Mat.* 23 47 (2006)

17. S Sudo, N Oshiki, N Shinyashiki et.al. *J.Phys. Chem.* A 111(16) 2993 (2007)

18. M Nakanishi, Ryusuke & Nozaki. *Physical Review* E 81 041501-6 (2010)

19. H Fellner-Feldegg. *J.Phys.Chem*. 73 616 (1969).

20. S Mashimo, T Umehara, T Ota, et.al. *J. Mol. liq.* 36 135 (1987)

21. RH Cole, JG Berberian, S Mashimo, et.al. *J. Appl. Phys*. 66 793 (1989).

22. D Bertolini, M Cassettari, G Salvetti, et.al. *Rev. Sci. Instrum*. 61 450 (1990).

23. A C Kumbharkhane, SM Puranik & SC Mehrotra. *J. Sol. Chem*. 22 12 (1992).

24. T Sato, R Buchner. *J. Mol. Liq*. 117 23 (2005)

25. S Sudo, N Shinyashiki, Y Kitsuki et.al. *J. Phys. Chem*. A 106, 458, (2002)

26. T Sato, A Chiba & R Nozaki. *J. Mol. Liq*. 101(1-3) 99 (2002)

27. T Sato, A Chiba & R Nozaki, *J. Mol. Liq*. 96–97 327 (2002)

28. S Mashimo, T Umehara & H Redlin *J. Chem. Phys*. 95, 6257, (1991).

29. R Pottel, K Giese & U Kaatze W.A.P.Luck; Weinheim : Verlag Chemie-Physik-Verlag, 391-407 (1974).

30. Kadam, S.S., Kanse, K.S., Joshi, Y.S. *et al. Indian J Phys* 92, 1367–1372 (2018).

31. SHINDE, M.N., TALWARE, R.B., HUDGE, P.G. *et al. Pramana - J Phys* 78, 297–308 (2012).

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